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GAS CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF TRACE QUANTITIES OF DIETHYL MALONATE IN ETHANOL

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This report presents an experimental study conducted to determine a method for analytically detecting and determining trace quantities of diethyl malonate (DEM) in ethyl alcohol using a gas chromatograph equipped with a flame ionization detector.

The method developed proved to be effective for determining trace quantities at a concentration (mean) range of 21-840 ng. A linear fit was obtained at this range with an average slope of $1.4032 \pm 0.0063 \times 10^{-7}$ ug/au and an intercept of 0.0359 ± 0.0359 ug. The correlation coefficient was 0.9996 ± 0.0009. Based on replicate injections, the accuracy of this method was within ±2.4%.

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PREFACE

The work described in this report was authorized under Project No. 1L162706A553F, CB Decontamination and Contamination Avoidance. This work was started in December 1985 and completed in April 1986. The experimental data are recorded in laboratory notebook no. 83-0122.

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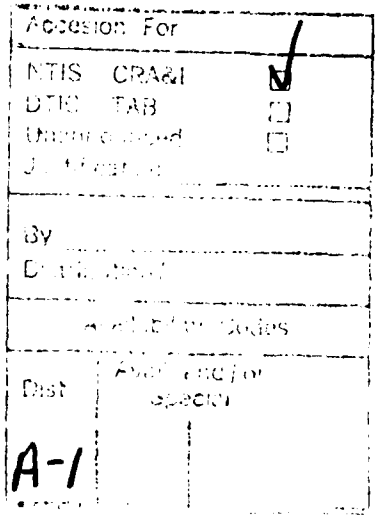

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1. INTRODUCTION

The objective of this work was to develop a method for detecting and determining trace quantities of diethyl malonate (DEM) in ethyl alcohol.

In the past, DEM has been used as a chemical agent simulant in decontamination, evaporation, dissemination, and persistency studies. The purpose for DEM's use was to support an experimental effort to determine the decontamination performance of a laboratory scale jet engine system. Coupon samples contaminated with DEM were exposed to a high velocity, high temperature air stream coming from the jet. Residual DEM on the coupons was extracted by immersion in an ethyl alcohol solution.

This report describes the development of an analytical procedure that allows the gas chromatographic/flame ionization detection and estimation of residual quantities of DEM on the decontaminated coupons.

2. EXPERIMENTATION

2.1 Equipment and Materials.

This experimental effort was performed on a Perkin Elmer gas chromatograph [GC (model Sigma 2000)] equipped with a flame ionization detector and employing the PE LCI-100 computer integrator.

Injections were performed manually using a Hamilton microliter syringe (series 700) with an accuracy within $\pm$1% of syringe capacity and repeatability to within $\pm$1% of dispensed volume.

The chromatographic columns tested were custom made by Perkin Elmer (Rockville, MD).

Ethyl alcohol (U.S.P., 200 proof) was used as the solvent. DEM, 99% pure, was obtained from Kay Fries Incorporated (Rockleigh, NJ) Lot # 82-0582.

2.2 Preliminary Considerations.

The primary objective of this effort was to increase the detection sensitivity for analyzing residual DEM on sample coupons after being exposed to a high velocity, high temperature gas stream.

An initial 10-mg load was to be deposited on the sample coupon. Sample jars filled with 10 mL of ethyl alcohol were to be used for extracting residual DEM on the tested plates.

The criteria used to select the sensitivity range was based on a minimum 20% evaporation (800 ng of DEM per milliliter of solution) and a maximum 99% evaporation of the initial 10-mg mass (20 ng of DEM per milliliter of solution).

2.3 Procedures.

2.3 1 Chromatographic Conditions.

The following chromatographic conditions were adopted for analytically determining DEM in ethanol. These conditions provided an acceptable separation of DEM from the solvent with a minimum running time of 7 min.

- Instrument: PE Sigma 2000
- Detector: FID
- Air Pressure: 20 psig
- Hydrogen Pressure: 20 psig
- Range: 1
- Column Temperature: 90 ^{o}C
- Injection Chamber Temperature: 250 ^{o}C
- Detector Temperature: 250 ^{o}C
- Carrier Gas: N2 (99.999% pure)
- Carrier Gas Flow Rate: 10 cm^3/min
- Column Material: 6 ft, 1/4 o.d. borosilicate glass
- Column Coating: 3% OV-101
- Column Support: Chromosorb WHP (100-120 mesh)

The computer integrator (LCI-100) conditions were as follows:

- Method: Area/Height %
- Starting Time: 0 min
- End Time: 7 min
- Peak Width at Base: 5.5-13.0 sec
- Sampling Rate: 3.13 pt/sec
- Area Sensitivity: 100%

- Base Sensitivity: 40%
- Skim Sensitivity: 0%
- Baseline Correction: Basepoint to Basepoint
- Chart Speed: 10 mm/sec
- Print Tolerance: 0
- Plotter Attenuation: X32
- Plot Offset: 5%
- Area/Height Rejection Threshold: 0

2.3.2 Calibration.

Two calibration curves were generated from known concentrations of DEM in ethyl alcohol.

Two standard solutions (0.42 µg/µL and 42 ng/µL) were prepared, and different volumes (0.5, 1.0, and 2.0 µL) were injected into the GC to enable calibration at the desired sensitivity range. To ensure repeatability of the DEM mass to peak area response, a minimum of four injections were performed per calibration point.

Tables 1 and 2 show the peak area response for the various weights injected. Table 3 shows the results of a trial study involving fixed volume (2 µL) injections with an automatic liquid sampler (PE AS-2000B) at a known concentration (0.42 µg/µL) to estimate the traceability of the method after performing the calibration procedure.

2.4 Results.

Statistical analysis and lineal regression were performed on the data collected for calibration.

Table 4 shows results for the mean, standard deviation, coefficient of variation, and uncertainty values at a 95% confidence level for each data point generated.

Results and analysis of each lineal fit are shown in Table 5. The analytical recovery data in Table 6 was obtained from the mean lineal fit curve in Table 5.

3. DISCUSSION

An average correlation coefficient of 0.9996 ± 0.0009 was obtained for a lineal fit of the calibration data. This coefficient is indicative of an acceptable lineal response at the stated conditions.

Table 1. Calibration Curve 1 for DEM in Ethyl Alcohol.

DEM Conc (μg/μL)	Target Weight (μg)	Injection Number	Injected Weight (μg)	Area Response (au)[1]	Normalized Area (au)[2]
0.42	0.84	1	0.88	5925898	5656539
		2	0.88	5972550	5701070
		3	0.84	5661404	5661404
		4	0.84	5675717	5675717
		5	0.84	5705550	5705550
	0.42	1	0.46	3064368	2797901
		2	0.46	2954041	2697168
		3	0.42	2746761	2746761
		4	0.46	3105206	2835188
		5	0.48	3199429	2799500
	0.21	1	0.25	1458912	1225486
		2	0.29	1681899	1217927
		3	0.25	1438893	1208670
		4	0.17	1010240	1247943
		5	0.21	1254278	1254278
0.042	0.084	1	0.082	236758	242532
		2	0.092	270632	247099
		3	0.084	242357	242357
		4	0.088	253422	241903
		5	0.084	245241	245241
	0.042	1	0.052	74029	59793
		2	0.046	65084	59424
		3	0.048	68794	60195
		4	0.042	61268	61268
		5	0.050	73282	61557
	0.021	1	0.027	44301	34456
		2	0.025	38463	32309
		3	0.023	36470	33299
		4	0.021	32947	32947
		5	0.021	33921	33921

[1]Area units.
[2]Areas were normalized to target weight mass.

Table 2. Calibration Curve 2 for DEM in Ethyl Alcohol.

DEM Conc (μg/μL)	Target Weight (μg)	Injection Number	Injected Weight (μg)	Area Response (au)[1]	Normalized Area (au)[2]
0.42	0.84	1	0.88	6002620	5729774
		2	0.82	5564680	5700404
		3	0.92	6452620	5891523
		4	0.86	5894070	5756999
	0.42	1	0.42	2713870	2713870
		2	0.42	2753140	2753140
		3	0.36	2370470	2765548
		4	0.42	2741250	2741250
	0.21	1	0.21	1213980	1213980
		2	0.21	1250330	1250330
		3	0.23	1329970	1214320
		4	0.19	1121630	1239696
0.042	0.084	1	0.097	302189	261689
		2	0.088	281803	268994
		3	0.084	206042	266042
		4	0.084	268034	268034
	0.042	1	0.053	81411	64514
		2	0.042	63865	63865
		3	0.059	91420	65079
		4	0.063	96317	64211
	0.021	1	0.027	48159	37457
		2	0.027	48062	37381
		3	0.025	46238	38840
		4	0.021	38410	38410

[1]Area units.
[2]Areas were normalized to target weight mass.

Table 3. Analytical Recovery of DEM from Ethyl Alcohol.

DEM		
Injected Weight (μg)	Replicate Number	Area Response (au)
0.84	1	5884799
	2	5730592
	3	5809521
	4	5764371
	5	5815551

Table 4. Statistical Analysis of Calibration Data.

DEM Confidence* Weight (μg)	Mean Area (au)	Standard Deviation (au)	Coefficient of Variation (%)	Limit ($\pm$au)
		Curve 1		
0.84	5680049	22414	0.4	27866
0.42	2775304	53856	1.9	66957
0.21	1230861	19550	1.6	24306
0.084	243826	2258	0.9	2797
0.042	60447	928	1.5	1154
0.021	33386	835	2.5	1038
		Curve 2		
0.84	5769674	84456	1.5	134215
0.42	2743452	22076	0.8	35101
0.21	1229581	18340	1.5	29161
0.084	266340	3368	1.3	5355
0.042	64417	515	0.8	819
0.021	38022	718	1.9	1142

*Based on a 95% confidence limit.

Table 5. Lineal Regression Analysis for Calibration Curves.

Curve (#)	Slope (µg/au)	Intercept (µg)	Correlation Coefficient
1	1.4037E-7	0.0387	0.9997
2	1.4027E-7	0.0331	0.9995
Mean	1.4032E-7	0.0359	0.9996
Conf. Limit	0.0063E-7	0.0359	0.0009

Table 6. Analysis of Analytical Recovery Data.

DEM Injected (µg)	Replicate Number	DEM Found (µg)	Mean (µg)	Standard Deviation (µg)	Confidence Limit (µg)
0.84	1	0 86	--	--	--
	2	0.84	--	--	--
	3	0.85	--	--	--
	4	0.84	--	--	--
	5	0.85	0.85	0.008	0.01

Calibration procedure results indicated that trace quantities of DEM in ethyl alcohol can be quantified within a coefficient of variation of 2.5%.

The traceability study for DEM in ethyl alcohol indicated an accuracy within 2.4% from known DEM concentrations.

4. CONCLUSIONS

Based on the experimental results, the use of a GC equipped with a flame ionization detector proved to be effective for determining trace amounts of DEM in ethyl alcohol at a concentration range of 21-840 ng.

A lineal fit was obtained at this range with an average slope of $1.4032 \pm 0.0063 \times 10^{-7}$ μg/au and an intercept of 0.0359 ± 0.0359 μg. The correlation coefficient was 0.9996 ± 0.0009.

Based on replicate injections at the 0.84-μg level, the accuracy of this method was within 2.4% (±0.02 μg).